Computational Approaches to the Development of Advanced Mercury Control Technologies

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The Need for Mercury Emission Control

- Mercury is a hazardous air pollutant of great public health concern.
- Coal-derived flue gases contain mercury (ppb-range) in the vapor-phase.
- Coal-fired power plants:
  - contribute one-third of the man-made mercury emissions in the U.S
  - emit more than 50 tons of mercury annually
  - are the single-largest source of man-made emissions.

- The EPA is working on a schedule for the regulation of mercury emissions that involves:
  - A final rule decided by 2004.
  - Expected compliance by 2007.
- Impending regulatory requirements are driving current research efforts to identify and develop efficient mercury control technologies.

Mercury Control and Computational Fluid Dynamics

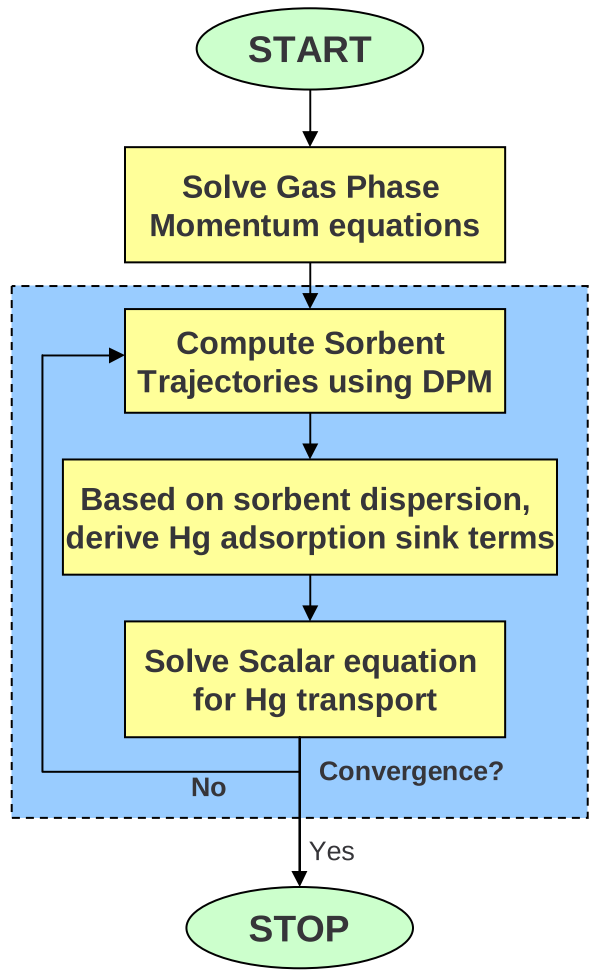
- **Project goal:** *Develop and validate a CFD-based methodology that can be used to understand sorbent-based mercury control processes.*

- **Approach taken:**
  - **Use framework of existing, unstructured CFD solver (Fluent).**
  - **Introduce scalar transport equation for gas phase mercury.**
  - **Implement mercury adsorption model for dispersed sorbent particles.**
  - **Couple adsorption model with mercury transport equation via source term.**
  - **In relevant cases solve for species transport using chemical kinetic mechanism for mercury oxidation (predict partitioning Hg^o / $HgCl_2$).**

- **Mercury control by sorbent injection is mass transfer limited**
  - **Work scope of current project is in-flight capture.**
  - **CFD provides detailed duct-scale information.**
    - Flue gas flow (local velocities, temperature, turbulence, speciation).
    - Sorbent dispersion in flue gas duct.

Modeling Approach

- Simulation of mercury capture as a Post-processing step.
  - Mercury species only present in trace amounts.
  - Mercury chemistry has negligible influence on concentrations of main flue gas constituents.
- Solve momentum equations for gas phase flow.
- Lagrangian modeling of particle phase.
  - Track sets of representative discrete particles by time integration of the equations of motion.
  - Particle sets may have an associated size distribution.
  - Solids and gas phase may exchange momentum, heat, and/or mass.
  - One-way coupling (gas to solid) exist for low particle loading => solid volume fractions <10%.
    - In the DOE sorbent injection field tests, the range of considered injection rates ensured very dilute flows amenable to one-way coupled simulation.



Mercury Adsorption Models

- **Pulverized activated carbon has a porous structure (pore radius 5 – 50 Å).**
  - **Large internal surface area (600 to 1,200 m^2/g) lends itself to efficient mass transfer.**

- **Adsorption takes place in three steps:**
  1. **Mass transfer from gas phase to external sorbent surface (boundary layer).**
     - Film resistance represented by a mass transfer coefficient.
  2. **Mass transfer through pore structure to interior of the sorbent particle.**
     - Diffusive transport, modeled with an efficient diffusion coefficient.
  3. **Surface adsorption on internal surfaces**
     - Adsorption equilibrium described by a Langmuir type isotherm.
     - Isotherm parameters calibrated based on fixed-bed experimental data.

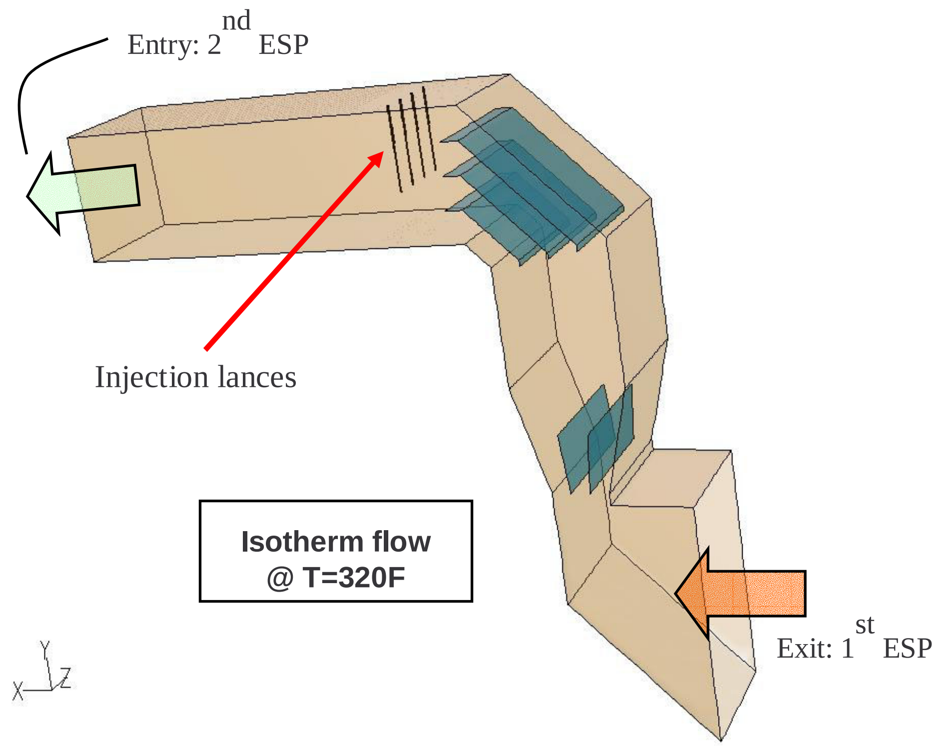
- **Mercury mass balance in the gas phase**
  - **Handled by a scalar convection-diffusion type equation.**

$$\frac{\partial}{\partial x_i}\left(\rho u_i \varphi - \Gamma \frac{\partial \varphi}{\partial x_i}\right) = S_\varphi$$

source term describes mercury adsorption

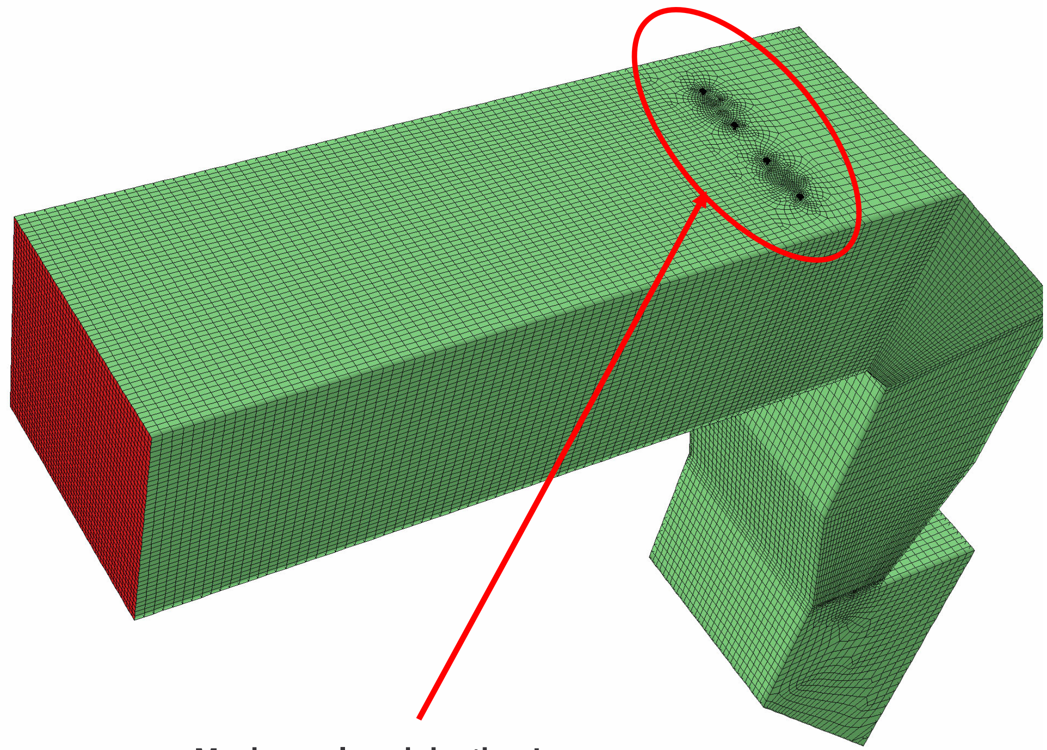
Simulation of Sorbent injection at Brayton Point Power Plant

- Sorbent Injection tests performed as part of the DOE/NETL mercury field test program.
- Power plant equipped with two electrostatic precipitators.
- Injection of activated carbon via set of eight lances upstream of the 2nd ESP.
- No mercury removal by fly-ash in the considered part of ductwork => pure in-flight capture !!
- Field tests showed good capture efficiency (~90%), in spite of short sorbent residence time (~0.5s)



Brayton Point Field Tests

Computational Model

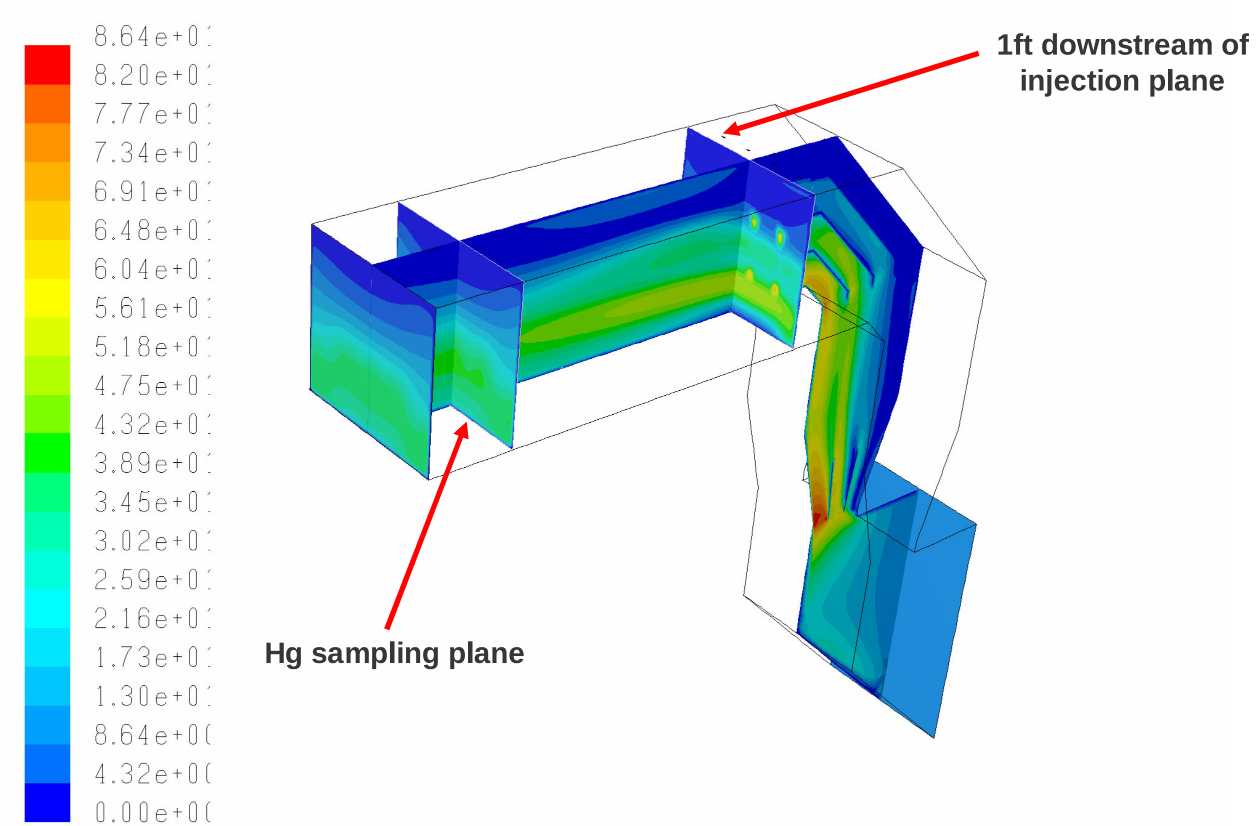


Mesh resolves injection Lances

- CFD model comprises the ductwork between two ESP units.
- The computational mesh consists of approximately 350,000 cells.
- High mesh quality ensured by predominant (90%) use of hexahedral cells.

Brayton Point Field Tests

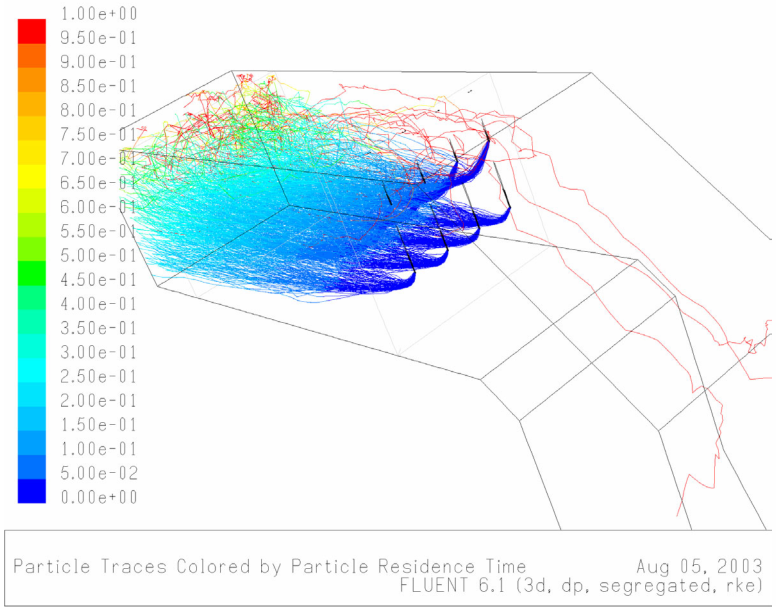
Simulated Gas Phase Flow – velocity magnitude plot

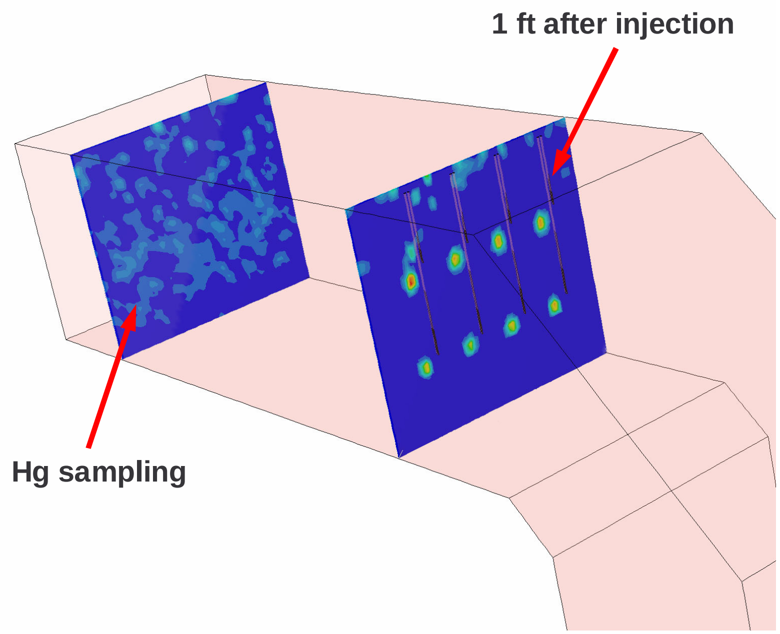


- Flue gas flow is badly distributed at the carbon injection plane
  - Caused by flow pattern at exit of plenum just downstream of first ESP unit.
  - Injection lances are long enough to penetrate separation zone ☺

Brayton Point Field Tests

Simulated Sorbent Dispersion





<u>Particle tracks</u>

<u>Particle concentrations</u>

- **Used stochastic tracking, which accounts for the effect of local turbulent fluctuations in a random manner.**
- **Injected particles had a uniform diameter of 20μm.**
- **A reasonable distribution of sorbent across the duct was predicted.**

Quantum Chemical Calculations

- ***ab initio* modeling of Hg + benzene and analogues**
  - **Activated Carbon:**
    - Unpromoted: *believed to be* physical adsorption
    - Promoted: *believed to be* physisorption and chemisorption
- ***ab initio* modeling of Hg oxidation by Cl, (O_3, other species)**
  - **complex reactions, what are fundamental steps?**

Computational Challenges With Hg

- **VDW → covalent → metallic w/size of Hg clusters**
  - **Subtle interplay between types of bonding**
  - **Requires method in which both are well described**
- **Ψ based methods (CC or QMC)**
- **Relativistic effects important**

Theoretical Methods

- HF
  - Will not model weakly bound systems.
- DFT
  - Well known deficiency for dispersion interactions.
- MP2
  - Far away from ccsd(t) and experimental result for Hg_2
- CCSD(T)
  - Good compromise, need adequate basis.
  - Our results obtained with CCSD(T) unless noted otherwise.
- MRCI
  - Might be necessary for certain interactions involving Hg.
  - Will weak interactions be modeled properly?

- MOLPRO - Mol Phys. 74, 1245 (1991).

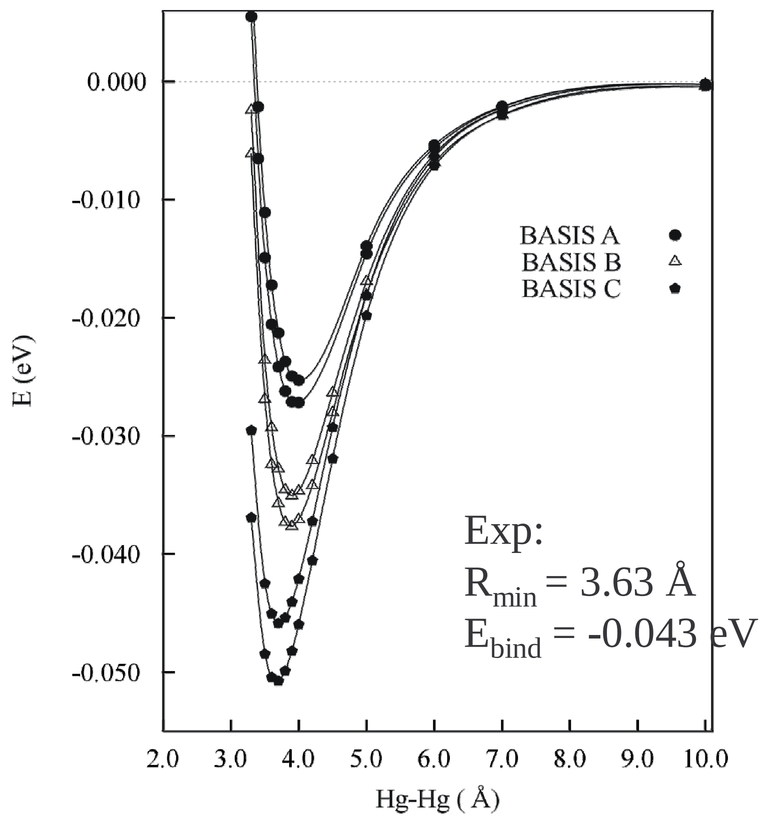
Stuttgart *ab initio* pseudopotential for Hg

- **Drastic reduction in computational cost**
- **Explicit treatment of only valence electrons**
  - **Ion core = core electrons (60 or 78) plus nucleus**
  - **Valence system treated in non-relativistic manner**
  - **All electron relativistic, quasirelativistic (Wood-Boring) or non-relativistic calculations used for Hg atom to generate the pseudopotentials**
- **Contributions of most important relativistic operators are (to some extent) transferred into the pseudopotential**
- **Core-valence correlation accounted for by semi-empirical polarization potential (cpp) for 78 e^- pp**

Nicklass, Dolg, Stoll, Pruess J. Chem. Phys. **102**, 8942 (1995).

Tests of Basis Sets on Hg_2

Hg_2 Potential Energy plot for three basis sets



Two curves shown for each basis;
upper curve counterpoise corrected.

- Basis Set A: (MOLPRO library)
  (4s4p1d)/[2s2p1d] → **13 fxns (0.25 min)**

  Kuechle, Dolg, Stoll, Preuss, Mol. Phys. 74, 1245 (1991).

- Basis Set B:
  (9s8p6d)/[8s6p3d] → **41 fxns (18 min)**

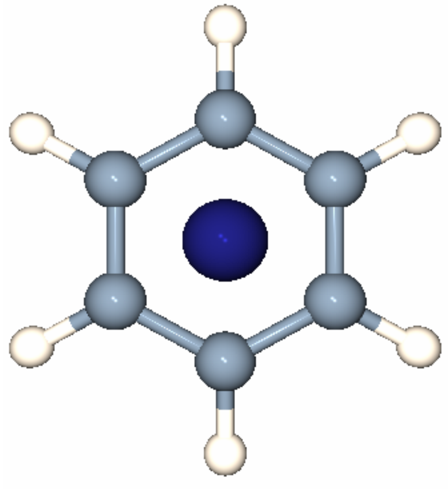
  Czuchaj et al. Chem. Phys. **214**, 277 (1997).

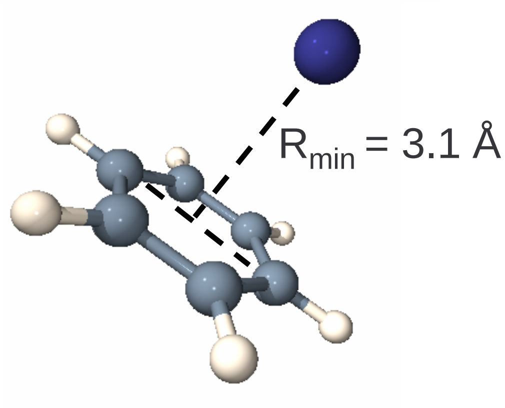
- Basis Set C:
  (6s6p5d3f1g) → **79 fxns (337 min)**

  Dolg and Flad J. Phys. Chem. **100**, 6147 (1996).

(Time is for calculation of PES for Hg_2)

Hg - Benzene Interaction



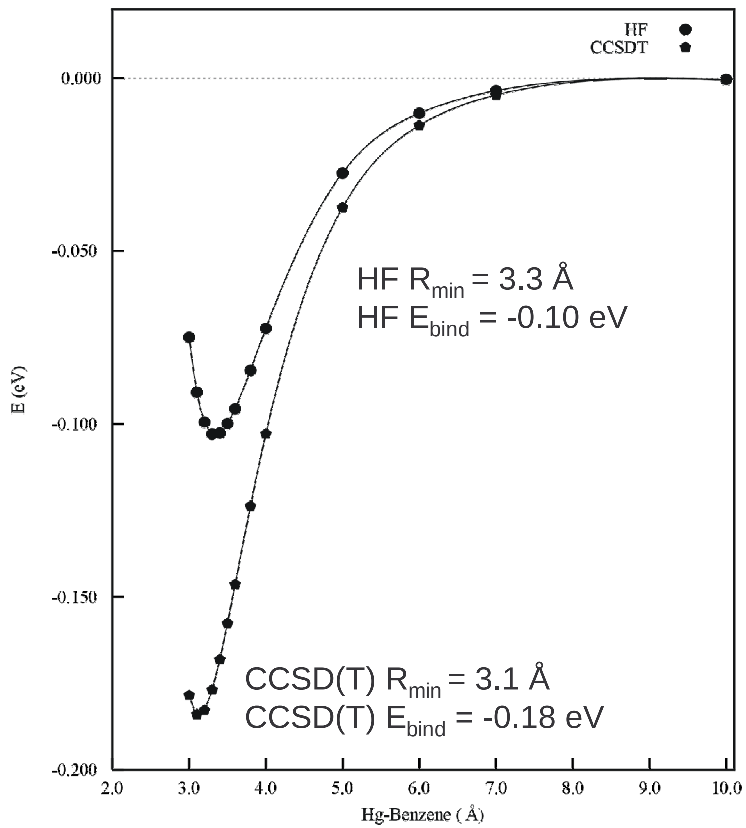


rC-C = 1.4148 Å

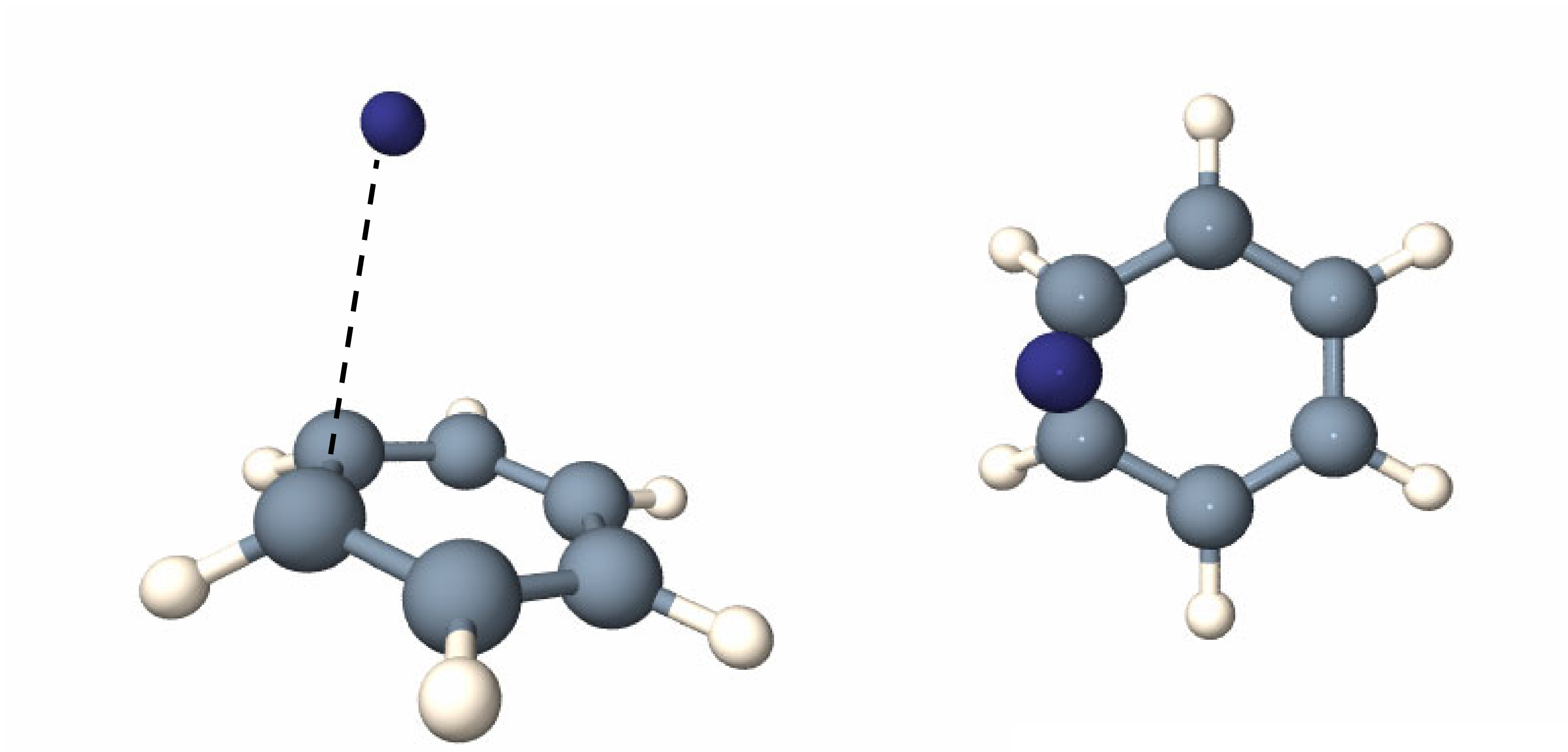
rC-H = 1.0795 Å

Potential Energy Plot

- Single Point Energy Calculations
- Hg basis set “A”, VDZ basis elsewhere
- Gas phase optimized coordinates for benzene

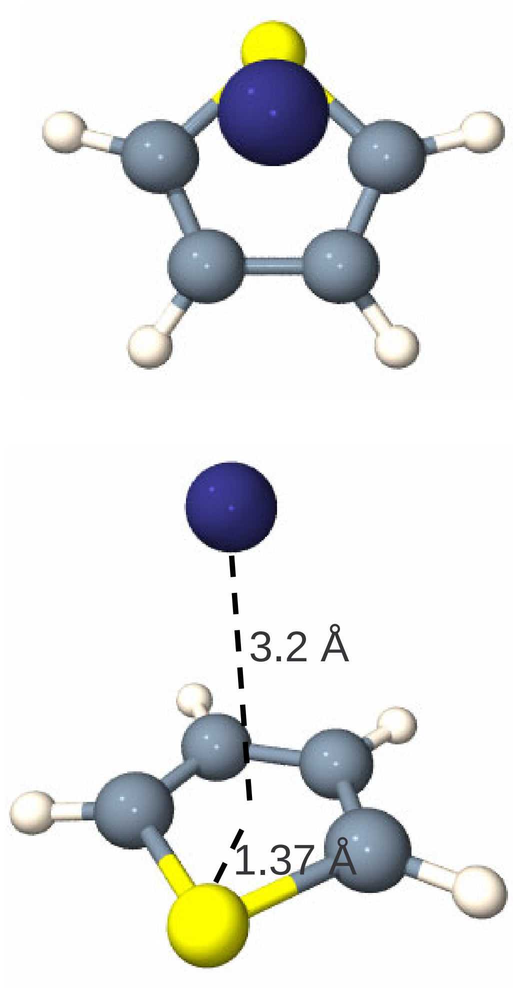


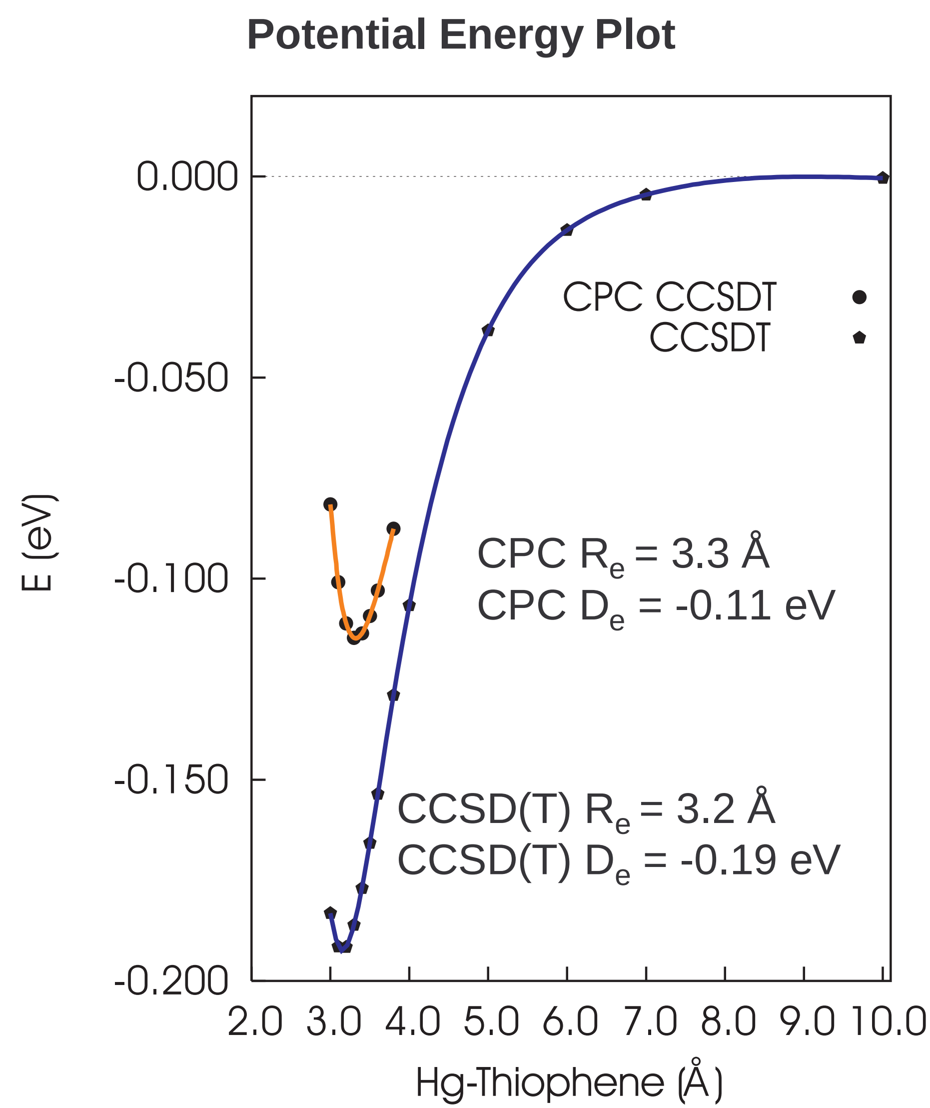
Hg - Benzene Edge Interaction



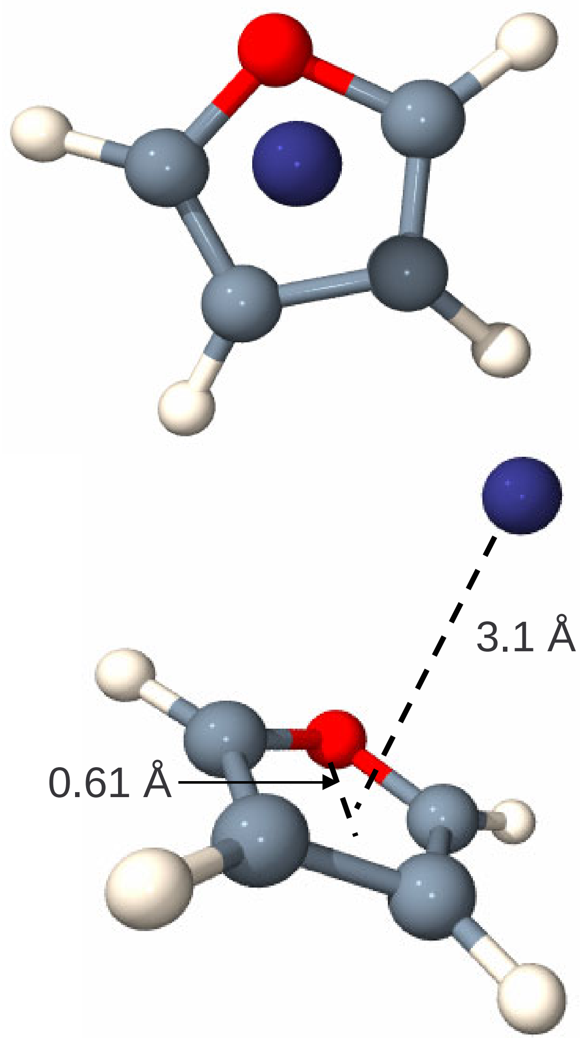
It has been speculated that this complex might exist, but we have not yet found a minimum for Hg interaction with the edge of the benzene molecule.

Thiophene and Hg

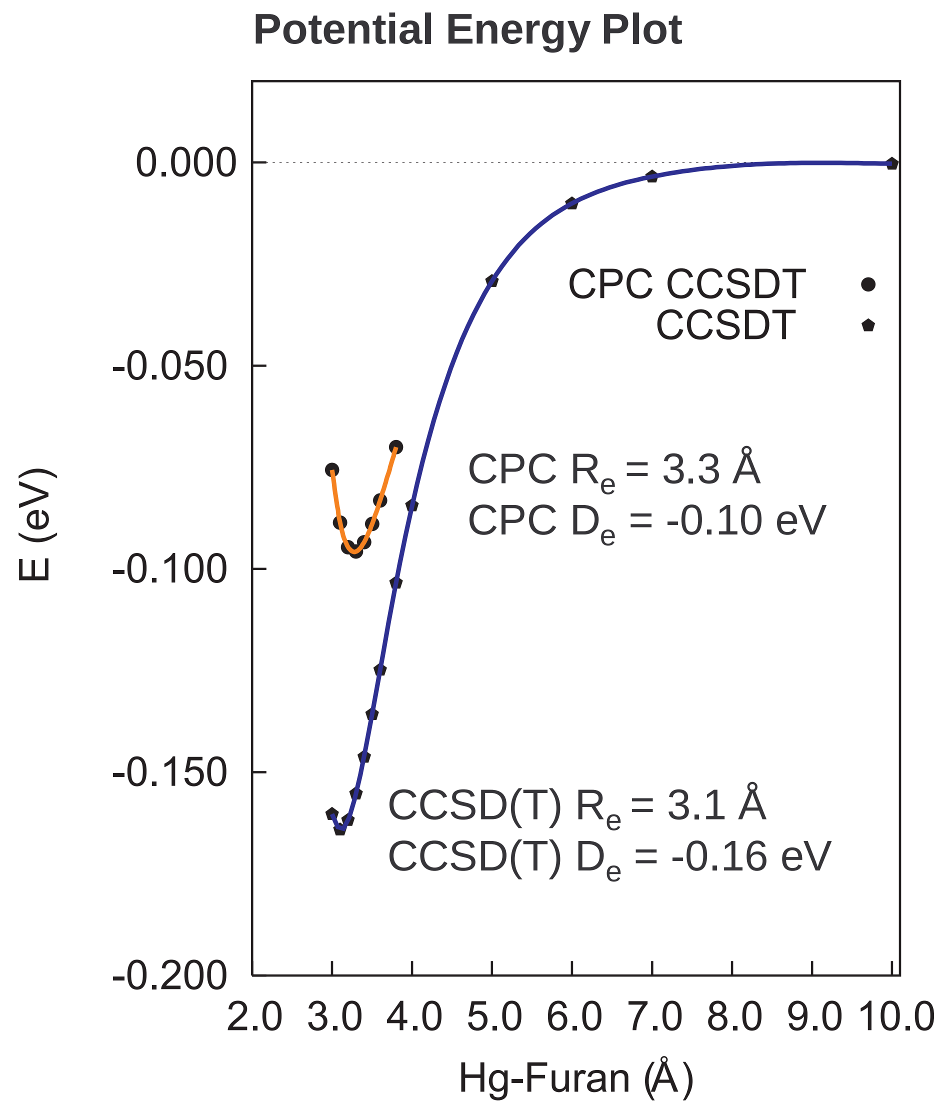




Furan and Hg



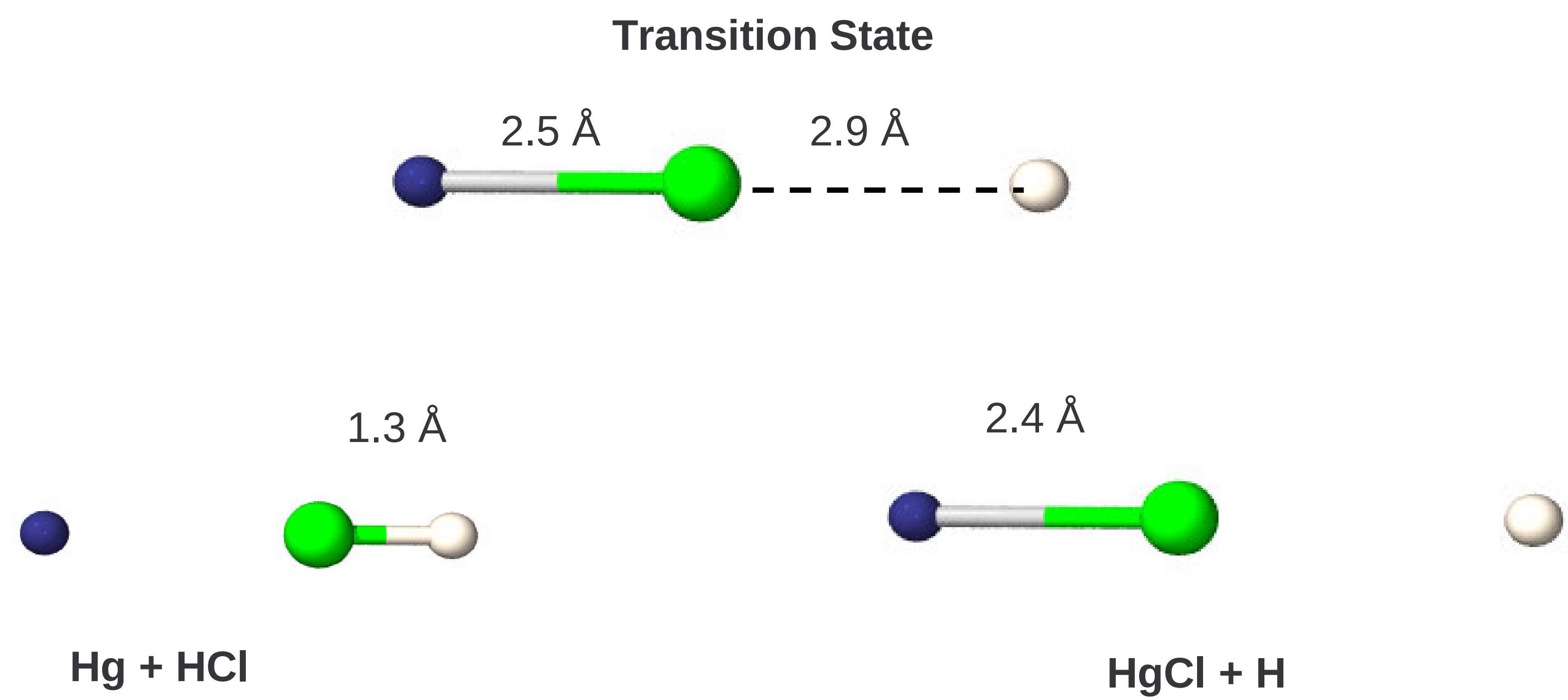
3.1 Å
0.61 Å



Potential Energy Plot
E (eV)
0.000
-0.050
-0.100
-0.150
-0.200
2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0
Hg-Furan (Å)
CPC CCSDT
CCSDT
CPC R_e = 3.3 Å
CPC D_e = -0.10 eV
CCSD(T) R_e = 3.1 Å
CCSD(T) D_e = -0.16 eV

Hg Oxidation

- The presence of HCl has been linked to the oxidation of Hg
- Details on molecular level (activation energies, rates) useful.



Conclusions

- **Computational Fluid Dynamics**
  - **Methodology can be useful for optimizing sorbent injection strategies**
  - **To lower operational costs.**
  - **To improve capture efficiency.**
  - **To predict effect of changing conditions (e.g. sorbent type) in advance.**

- **Quantum Chemistry**
  - **Weak interaction predicted between Hg and benzene, furan and thiophene; consistent with physisorption.**
  - **We do not find an edge-bonded Hg-benzene complex.**
  - **E_{bind} ~0.1 eV using limited basis set for Hg.**
  - **Extrapolate E_{bind} ~0.2 eV using better basis set for Hg.**
  - **Heteroatom does not influence the interaction.**

Future Directions

- Computational Fluid Dynamics
  - Finish implementation of mercury adsorption model
  - Model validation using lab- and pilot-scale experimental data
  - Consider modeling of mercury capture in fabric filters
  - Use properties predicted by quantum chemistry calculations

- Quantum Chemistry
  - Locate (or rule out) edge-bonded Hg-benzene complex
  - Employ larger basis set on Hg-benzene complex to improve estimate of E_{bind}
  - Coupled cluster calculations for oxidation of mercury
  - Predict rates useful for modeling and/or molecular dynamics (e.g. CFD)